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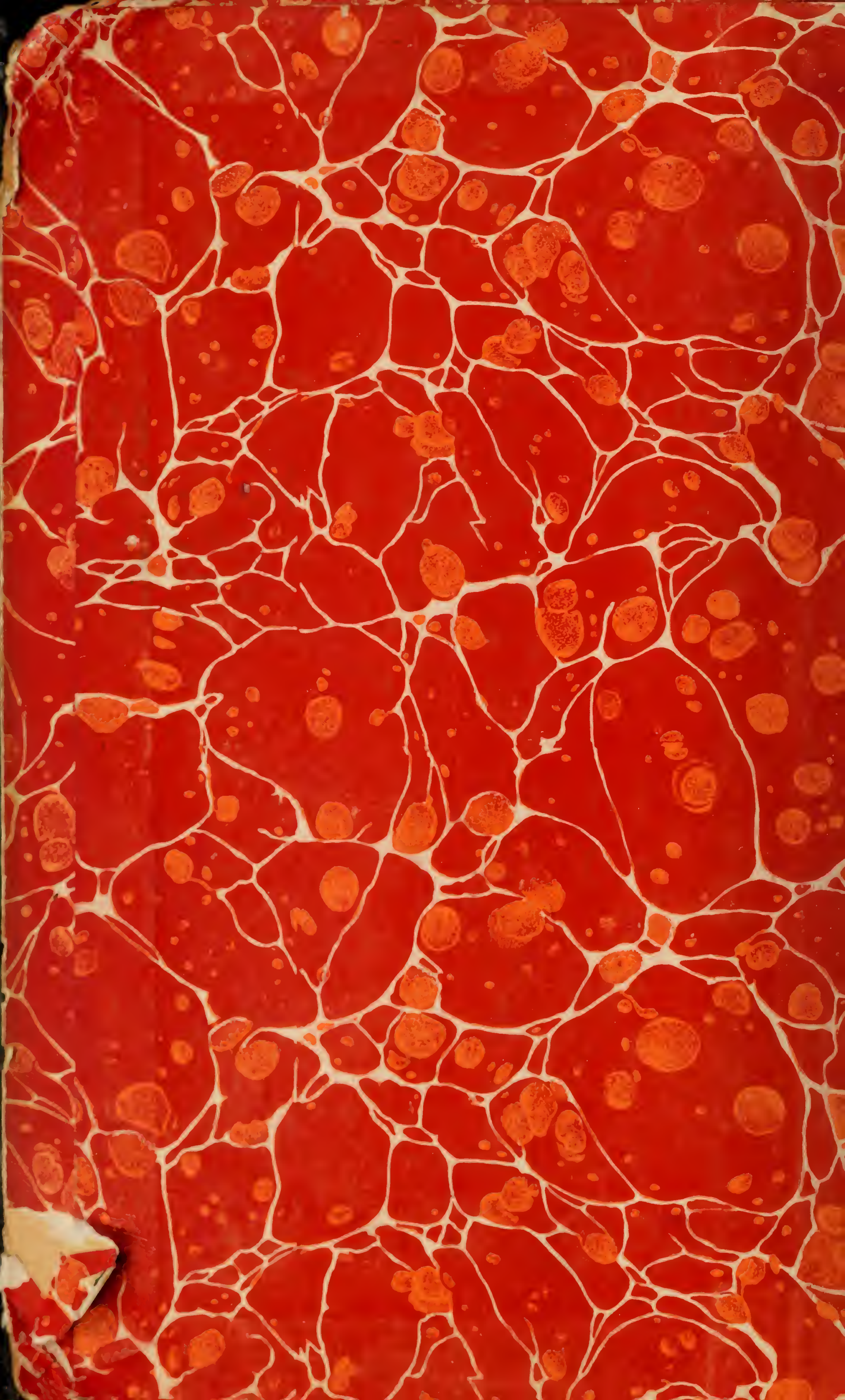

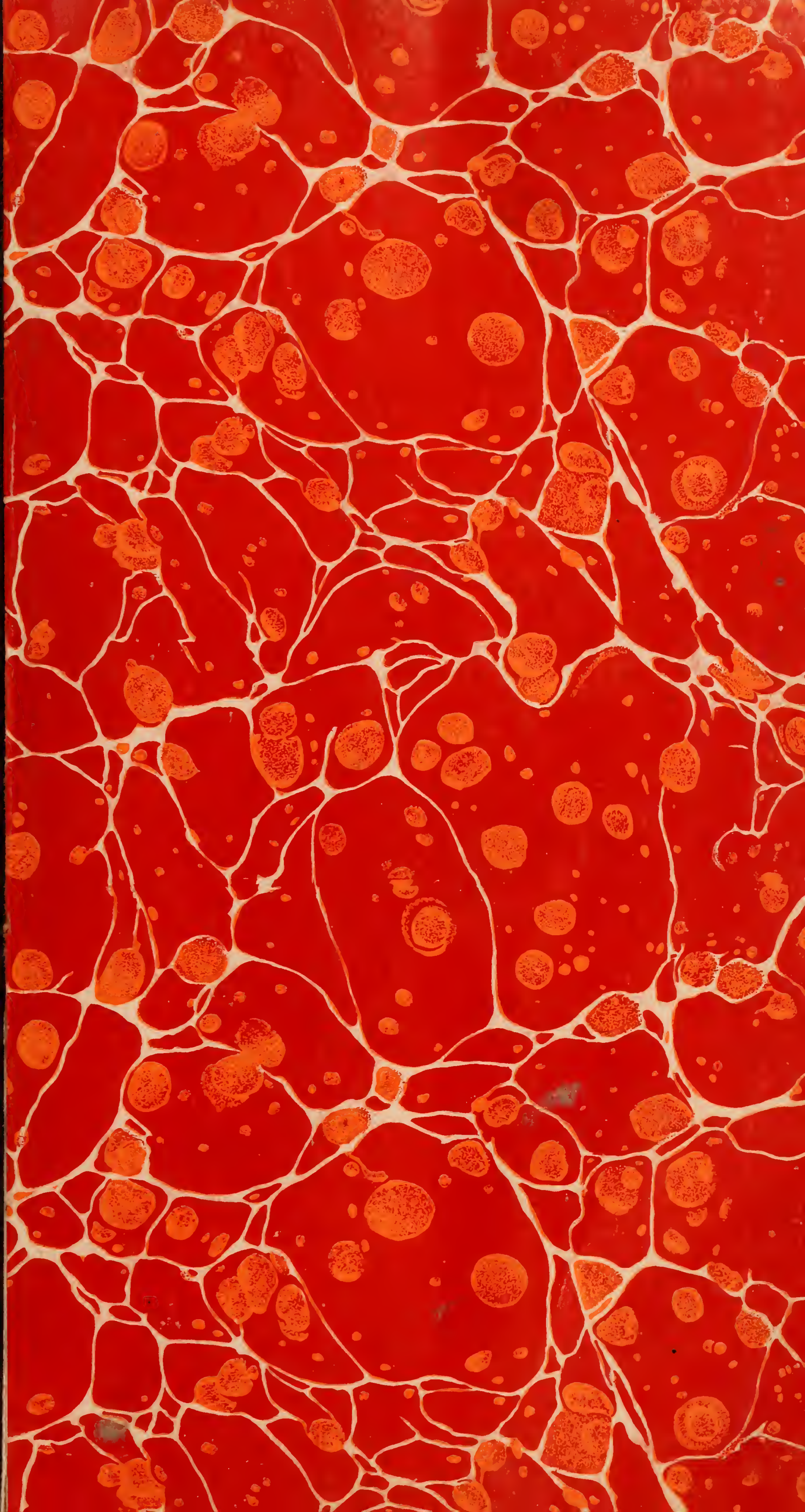

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COMPOSITION OF GRIDS FOR POSITIVE PLATES OF STORAGE BATTERIES AS A FACTOR INFLUENCING THE SULPHATION OF NEGATIVE PLATES

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ABSTRACT

The conditions under which antimony, a constituent of battery grids, may produce detrimental effects in the operation of storage batteries have generally been regarded as exceptional. Recent experiments at the Bureau and elsewhere have shown, however, that the corrosion of the grids of positive plates, under normal operating conditions, may liberate antimony from the alloy in sufficient amounts to affect the operation and life of the negative plates. Two series of cells were prepared and operated in the laboratory to study the effect of varying the composition of the grids for positive plates. The first series included all cells having lead-antimony grids and the second included cells having positive grids containing various percentages of cadmium. Data on the capacity of these cells during 115 cycles are given, together with measurements of plate potentials, rate of sulphation, and the chemical analysis of the active material of negative plates for antimony.

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I. INTRODUCTION

Antimony, when present in the active material of negative plates of storage batteries, is a cause of local action which results in the formation of lead sulphate and the liberation of hydrogen. Jumau[1] mentioned antimony as a cause of excessive sulphation of negative plates in a paper published in 1898 and 2 years later Strasser and Gahl[2] showed that hydrogen is liberated more easily on antimony than on lead. The rapid local action which is produced when freshly charged negative plates are immersed in electrolyte containing as little as 0.001 percent of antimony sulphate was measured quantitatively by Vinal and Schramm.[3]

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[1] Ecl. Electr., vol. 16, p. 133, 1898.
[2] Zs. Elektrochemie, vol. 7, p. 11, 1900.

Lead alloyed with antimony has been used for making the grids of pasted plates since Sellon[4] patented a grid of such material for storage batteries more than 50 years ago. His invention proved to be an important step in the development of storage batteries, since this alloy has good casting qualities and is stronger and less subject to corrosion than pure lead. Because of these and other desirable qualities, lead-antimony alloys have been used almost exclusively for making grids.

The antimony in the grid metal is not a source of serious local action at the negative plates, provided the antimony remains in the grids and is not deposited on the active material. Any antimony in the electrolyte, whether it comes from the grids or is present as an impurity from some other source, has been found to deposit on the active material of the negative plates. Analyses of electrolyte from batteries which have been in service seldom reveal appreciable amount of antimony, but analyses of the active material of the negative plates have shown one half percent or more of antimony in the surface layers. Jumau[5] found 40 percent of the antimony to have been deposited within 0.1 mm from the surface of the plate and 99 percent of the total in a layer of active material 1 mm deep. More recently Barrett,[6] who used the X-ray spectrograph to study the crystalline structure of lead sulphate, reported finding numerous lines from antimony and other unidentified crystals in the active material of discarded battery plates.

Conditions under which antimony may produce detrimental effects have generally been regarded as exceptional, but recent experiments by Crennell and Milligan[7] and by Schubert[8] as well as tests made at the Bureau of Standards have demonstrated that corrosion of the grid structure of positive plates, even in normal operation, may supply antimony to the negative plates in sufficient amounts to affect seriously their performance. During each period of charge, antimony from the positive grids is deposited in minute amounts upon the negative plates. It accumulates there and increases the rate of sulphation of these plates.

Crennell and Milligan have stated that there is no relation between the amount of antimony which is present in the active material and the rate of sulphation produced, because successive charges and discharges of the battery cover the antimony with lead or lead sulphate and thereby decrease its effect. Freshly deposited antimony is, however, very active, as the results of Vinal and Schramm have shown. This is to be expected because the overvoltage for hydrogen discharge on antimony is lower than on lead by 0.11 volt[9] or more.[10]

Other alloys of lead have been proposed at various times and some of these have been used in storage batteries to a limited extent. The

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[3] J.Am.Inst.Elec.Eng., vol. 44, p. 128, 1925.
[4] British patent 3987 of 1881, French patent 147831 of 1882.
[5] Les accumulateurs Electriques, p. 350, 1907.
[6] J. Ind. & Eng. Chem., vol. 25, p. 298, 1933.
[7] Trans. Faraday Soc., vol. 27, p. 103, 1931.
[8] Paper read before National Battery Manufacturers Association Apr. 24, 1931.
[9] See footnote 7.
[10] See footnote 2, p. 795.

James[11] form of storage battery made use of an alloy containing 1 percent cadmium for the positive grids and 2 percent antimony for the negative grids. The Knowles[12] battery employed an alloy of 82 percent lead, 16 percent tin, 1.9 percent antimony, and 0.1 percent arsenic. The Worms[12] battery, 1892, used an alloy of 96.5 percent lead, 2.2 percent antimony, and 1.3 percent mercury. Grids for Julien[12] plates were made of 92 percent lead, 4.5 percent mercury, and 3.5 percent antimony. More recently patents have been issued for other compositions. An alloy of lead and barium was patented[13] in Germany in 1917. In 1923 Heil patented[14] a lead-cadmium alloy containing 2½ percent cadmium. Hagen[15] also patented a lead-cadmium alloy. LaRoche[16] patented an alloy of lead, nickel, silver, and cadmium, and Heil[17] patented a composition of lead with 0.5 per cent cadmium and 1 percent mercury. Gardner[18] patented a composition of lead and molybdenum and Kawakami[19] patented a composition of lead, antimony, and mercury. Alloys of lead and bismuth have been tried at the Bureau of Standards and by Schubert.[20]

Few data are available about the performance of grids made from these alloys. Obviously there is little to tempt the manufacturer to change from the established alloys of lead and antimony except as some other composition may be shown to be definitely superior.

It is not the purpose of this paper to advance claims for unusual compositions or new alloys, but rather to report the results of tests which have been made, showing the limitations imposed on the negative plates by antimony coming from the positive grids. Corrosion of the positive grids occurs slowly in the normal operation of a battery, and the service of the battery may extend over a long period of years. The Bureau has been called upon, however, to examine batteries in which more severe corrosion of the grid structure of the positive plates has caused the failure not only of these but the failure of the negative plates as well by excessive sulphation.

The experiments reported in this paper deal with batteries containing positive plates having grids made of lead-antimony alloys of varying composition and other batteries containing positive plates having grids of lead-cadmium alloys. The capacity of the individual cells was measured during 115 cycles of charge and discharge following which tests for the retention of charge were made. The rate of sulphation of the negative plates was determined by a method which has been described[21] previously. Significant changes in the charging potential of the negative plates were observed during the course of the work and these are compared with measurements on experimental cells to which portions of antimony were added. Analytical determinations of the amount of antimony present in the negative active material were made at the conclusion of the work.

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[11] Electrician, vol 26, p. 751, 1891.
[12] The Storage Battery, by Treadwell, p. 51.
[13] German patent, 301380 of 1917.
[14] German patent, 385651 of 1923.
[15] German patent, 482061 of 1928.
[16] British patent, 119100 of 1918.
[17] British patent, 209749 of 1924.
[18] U.S. Patent, 938312 of 1909.
[19] U.S. Patent 1575167 of 1926.
[20] See footnote 8, p. 796.
[21] B.S.Tech. Paper no. 225, 1922.

II. PREPARATION OF THE EXPERIMENTAL PLATES

1. GRIDS

Grids of various alloy compositions were used in making the positive plates. Since most of the desired compositions were not available commercially, it was necessary to prepare these alloys and cast the grids in the laboratory. A few commercial grids were included in the experiments for comparison with the laboratory product. All of the grids were 5⅝ inches wide, 4⅞ inches high, and ⅛ inch thick. The grids cast in the laboratory differed in design from the commercial grids in having 27 horizontal crossbars (exclusive of the frame), while the commercial grids had 36 horizontal crossbars. This difference may explain some of the variations in performance of the cells as will appear in later paragraphs.

Grids for negative plates were all commercial grids of the same composition, since no question of the corrosion of these grids is involved.

The results of the work have been divided into two series of experiments. The first, called the antimony series, includes measurements on cells for which the positive grids were of lead alloyed with antimony in amounts ranging from 0 to 12 percent of antimony. The second series, called the cadmium series, includes results on all cells whose positive grids contained cadmium. The percentages of cadmium varied from 0.25 to 2 percent and several of these alloys also contained small percentages of antimony, since the casting qualities of the lead-cadmium alloys appeared to be improved by the addition of the antimony. The compositions of the various alloys is shown in tables 1 and 7. The materials used were refined grades of lead and antimony. The cadmium was part of the supply used for making standard cells.

2. PASTING THE PLATES

The grids were pasted in the laboratory, using nearly identical formulas for both positive and negative plates. This was done in order to avoid unnecessary variations in the materials employed. For the positives, litharge, having properties described below, was mixed with sulphuric acid, 1.100 specific gravity, in the proportion of 100 ml of solution per kilogram of oxide, and to the mix a small quantity of water was added to control the consistency of the paste. The same formula was employed for the negative plates with the addition of three eighths percent of lampblack. Mixing was done in a lead-lined mixing machine.

The properties of the oxide, determined by methods previously described,[22] were as follows:

Apparent density (Scott volumeter figure)	32. 5
True density	9. 54
Red lead content ——percent	. 8
Acid absorption ——mg/g	80
Fineness:	
Cone 1 (Thompson classifier) ——percent	29
Cone 2 ——do	17
Cone 3 ——do	15
Cone 4 ——do	12
Cone 5 ——do	27

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[22] Vinal, Storage Batteries, 2d ed., pp. 20–21.

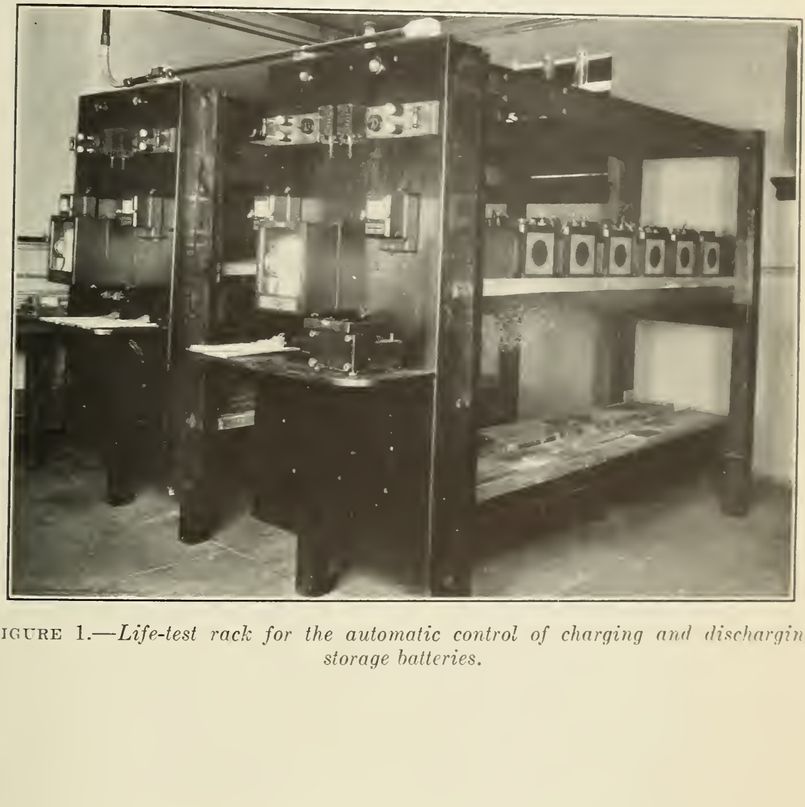

Figure 1.—*Life-test rack for the automatic control of charging and discharging storage batteries.*

After pasting, the plates were pickled for 20 hours in sulphuric acid having an initial specific gravity of 1.150 at 25° C.

3. FORMATION OF THE PLATES

Because of the various compositions of the grid metal, it was not advisable to form all the plates together. The plates were assembled, therefore, into groups according to the kind of grids. Separators of Port Orford cedar were inserted and the elements placed in individual jars. Each cell contained 5 positive plates and 6 negative plates.

Formation proceeded nearly uniformly in all cells, and no significant differences in the potentials of the positive plates were observed as a result of the differences in composition of the grids in these plates. At the conclusion of formation the cadmium readings on the positive plates were all within 0.01 volt of the value 2.45 volts, the current at this time being 2.1 amperes. Cadmium potentials of negative plates ranged from −0.13 to −0.09 volts. The more negative readings were obtained for plates in the cells whose positive grids contained the least amount of antimony.

III. APPARATUS FOR CHARGING AND DISCHARGING THE CELLS

The cells were charged and discharged automatically during 115 cycles except as the automatic control was omitted at intervals in order to determine the capacity of the individual cells to a final voltage of 1.75 volts per cell at the 5-hour rate.

The automatic control for making life tests of storage batteries has been in operation at the Bureau since 1930. This equipment, part of which is shown in figure 1, has not been described previously.

The essential parts of the equipment are:

1. *Time-controlled programs of charge and discharge.*—The clocks employed for these tests are the same as for the automatic testing of dry cells.[23] An additional program machine was provided for the storage-battery tests and the following schedule adopted:

4 p.m. charging begins.
7 a.m. charging ends.
10 a.m. discharging begins.
3 p.m. discharging ends.

When the program machine made contact at the time for charging to begin a latching relay was closed and this in turn closed the switch of the charging circuit and held it closed for a period of 15 hours when a second contact on the program machine unlatched the relay and terminated the charge. The discharge circuit for the batteries was operated as a separate circuit in a similar manner.

2. *Regulation of the current during charge and discharge.*—The current was adjusted initially to the proper value by inclosed carbon rheostats, one being provided for the charging circuit and a separate rheostat for the discharging circuit. The current for discharge was held constant automatically by the use of ballast resistance tubes consisting of iron filaments in an atmosphere of hydrogen. The particular tubes were rated for 6½ amperes so that two in parallel main-

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[23] Commercial Standards Monthly, vol. 7, p. 37, 1930.

tained a current of 13 amperes, which is about the 5-hour rate for these batteries. The essential characteristic of these ballast tubes is their ability to maintain a constant current, although the voltage at the terminals of the tubes may vary from 10 to 30 volts. This allowed for variations in the voltage of the batteries during discharge, and no manual regulation was required. The current was held constant to within about 1 percent. Similar arrangements were available for charging the batteries, but the ballast tubes were not always used in the charging circuit because the cells could be charged satisfactorily without them.

3. *Recording meters.*—The electrical input and the output of the batteries were measured by ampere-hour meters mounted on the panels of each test rack. These can be seen in figure 1 to the right and left of the recording ampere-hour meter which is in the center of the panel. When measured discharges were made the current was indicated by an ammeter. The voltages of the individual cells were recorded and in addition the potentials of the positive and negative plates were measured with the cadmium electrode. The algebraic difference of the cadmium potentials of the positive and negative plates agreed with the measured cell voltage to within 0.01 volt in nearly all determinations. However, the presence of cadmium in the electrolyte of some of the cells as a result of corrosion of grids containing cadmium makes the readings with the cadmium electrode on such cells of doubtful value. We have given in this paper the cadmium potentials of the negative plates for the antimony series of experiments only.

IV. ANTIMONY SERIES OF EXPERIMENTS

1. CAPACITY DETERMINATIONS

The cells were connected in series and their capacities, voltages, and plate potentials were observed during 115 cycles of charge and discharge. Table 1 gives the results of measurements for 6 cycles at intervals during the course of the work, together with the composition of the grids of the positive plates in each cell. The capacity of each cell increased slowly. Cells A, B, and C, which contained grids having the least antimony, were not in as good condition as the others when the plates were examined at the end of the hundredth cycle. The pure-lead grids of the positive plates, cell A, were badly corroded and expanded and a short circuit was removed. Cell B was in about the same condition. Cell C had positive plates that were definitely better than in cells A and B, but one grid was cracked. All the other cells were in satisfactory condition.

TABLE 1.—*Capacity during 113 cycles of charge and discharge*

[Ampere-hours at the 5-hour rate]

Cell	Composition of positive grids		Cycle no. 2	Cycle no. 23	Cycle no. 49	Cycle no. 78	Cycle no. 91	Cycle no. 113	Condition of positive plates
	Lead	Antimony							
	Percent	*Percent*							
A	100	0	40	63	68	69	70	72	Corroded, expanded, and cracked.
B	99	1	47	65	68	74	75	68	Do.
C	97	3	53	63	66	72	70	74	1 grid cracked.
D	93	7	49	64	68	70	72	74	Good.
E	91	9	49	64	68	72	74	76	Do.
F	88	12	42	64	70	72	74	76	Do.
T	90	10	49	66	70	74	75	76	Do.
U	90	10	56	66	70	74	77	76	Do.
V	90	10	44	66	70	73	77	76	Do.

The table shows that the three cells, T, U, and V, which contained the commercial grids exceeded most of the others in capacity. This may have been the result of slightly greater amount of active material in these plates compared with the others. The general conclusion to be drawn from the results in table 1 is that no large differences in capacity resulted from variations in the antimony content of the positive grids.

2. LOSS OF CAPACITY ON OPEN CIRCUIT

Following the capacity measurements the cells were tested for loss of charge during 114 days. They remained on open circuit for this period at room temperature. The results are given in table 2. Cell B failed completely. The other cells, from A to F, showed increasing loss of charge as the percentage of antimony in the positive grids was increased. The capacity of the cells, however, was limited by the negative plates (except for cell A whose positives were badly corroded and expanded). The cells T, U, and V, containing the commercial grids, suffered a greater loss of charge than the others. It will be shown in table 5 that more antimony had been deposited on the negative plates of these cells.

TABLE 2.—*Retention of charge during standing test of 114 days*

Cell	Composition of positive grids		Loss of charge during 114 days	Remarks
	Lead	Antimony		
	Percent	*Percent*	*Percent*	
A	100	0	46	Positives limited capacity.
C	97	3	46	Negatives limited capacity.
D	93	7	54	Do.
E	91	9	59	Positives and negatives equal.
F	88	12	62	Negatives limited capacity.
T	90	10	70	Do.
U	90	10	72	Do.
V	90	10	70	Do.

3. CHANGES IN PLATE POTENTIALS

In table 3 the charging voltages and cadmium potentials of the negative plates are given. With few exceptions, the cell voltage was found to be lower and the negative plates less polarized in cells having the larger amounts of antimony in the positive grids. The high value of voltage for cell A (in which no antimony was present in the positive grids) is attributable to the high polarization of the negative plates. This is in marked contrast to cell F. The cadmium potential measurements on the positive plates of these two cells were the same within 0.01 volt. The results in table 3 show a decrease in the polarization of negatives for all cells having positive plates containing antimony.

Table 3.—*Changes in potential of the plates during 115 cycles*

[Values in volts at end of charging periods]

Cell	Composition of positive grid		Cycle 1		Cycle 23		Cycle 50		Cycle 115	
	Lead	Antimony	Cell	Negative Cd	Cell	Negative Cd	Cell	Negative Cd	Cell	Negative Cd
	Percent	*Percent*								
A	100	0	2.61	−0.15	2.74	−0.24	2.79	−0.24	2.82	−0.25
B	99	1	2.62	−.14	2.72	−.23	2.75	−.23		
C	97	3	2.63	−.13	2.73	−.22	2.76	−.24	2.60	−.10
D	93	7	2.61	−.13	2.71	−.22	2.73	−.22	2.59	−.06
E	91	9	2.60	−.12	2.69	−.20	2.73	−.21	2.53	−.02
F	88	12	2.57	−.11	2.67	−.19	2.71	−.19	2.56	−.02
T	90	10	2.60	−.13	2.69	−.19	2.70	−.16	2.52	.00
U	90	10	2.60	−.12	2.69	−.19	2.69	−.16	2.52	−.02
V	90	10	2.60	−.14	2.69	−.19	2.70	−.17	2.54	−.02

As a further test of the effect of antimony on the polarization of the negative plates, four negative plates were placed in separate containers with pure-lead positives and subjected to a prolonged charge (table 4). Two of the negative plates had been in active service 2 years; the others were previously unused. Cadmium readings on the positive plates all show a remarkable uniformity, but quite the contrary is true for the negative plates. Plates which had been in service previously did not reverse in potential to the cadmium electrode, as was observed in the case of unused plates.

Table 4.—*Effect of antimony on charging voltages and cadmium potentials*

[Specific gravity of electrolyte 1.190 at 25° C.]

[Negative plates of same make and type charged against pure-lead positives]

No.	Condition of cell	Voltage of cell	Positive cadmium potentials	Negative cadmium potentials
		Volts	*Volts*	*Volts*
1	Negative plates after 2 years' service	2.51	2.49	0.00
2	do	2.49	2.50	+.02
3	Unused negative plate	2.64	2.49	−.13
4	do	2.63	2.49	−.16
4	Unused negative plate, first portion of antimony added	2.51	2.49	−.05
4	Unused negative plate, second portion of antimony added			−.03
4	Unused negative plate, third portion of antimony added	2.54	2.50	−.01
4	Unused negative plate, fourth portion of antimony added	2.53	2.50	.00

After steady readings had been obtained, four portions of antimony were added to one of the cells (no. 4), and a decrease in polarization of the negative plates in this cell was observed while the charging current was maintained at its previous value. The antimony was added in the following manner: 100 ml of electrolyte was withdrawn from the cell, which contained a total of 700 ml of electrolyte. The portion withdrawn was saturated with antimony sulphate, $Sb_2(SO_4)_3$, filtered and returned to the cell. The three remaining portions were added, similarly, at intervals of one half hour, except that 50-ml portions were employed. The total amount of antimony added was small. Determination of the antimony, Sb, in solutions similarly treated indicated that the total amount added to the cell was probably less than ¼ g.

The cell voltage and cadmium potentials of plates in the cell to which antimony was added were unchanged on the following day. This was true also of the other cells to which antimony had not been added.

4. DETERMINATION OF ANTIMONY IN THE PLATES

Analytical determinations of antimony in the surface layers of active material of the negative plates were made after the completion of the sulphation tests reported in the next section. It is desirable, however, to present the analytical determinations before giving the results of the sulphation measurements.

After removing the negative plates from their respective solutions in the sulphation apparatus they were allowed to dry without washing. Samples of the surface material, which was largely lead sulphate, were removed with particular care to avoid including in the sample any portion of the grid material. Samples of about the same weight were removed from the same surface area of each plate in order that the depth of the removed layer should be approximately the same for each plate. The weight of each sample is given in table 5.

TABLE 5.—*Determination of antimony in active material of negative plates after 115 cycles against positive plates having grids containing various percentages of antimony*

Cell	Composition of positive grids		Weight of sample negative active material	Antimony found in active material	Average
	Lead	Antimony			
	Percent	*Percent*	*g*	*Percent*	*Percent*
A	100	0	1.08 1.17	0.04 .04	0.0
C	97	3	1.04 1.20 .91	.12 .11 .09	.1
D	93	7	.98 1.15	.25 .23	.2
E	91	9	1.47 .97 1.07	.25 .27 .26	.2
F	88	12	.99 1.09	.33 .31	.3
T	90	10	1.11 1.21	.50 .42	.4
V	90	10	1.22	.41	.4

The analytical procedure was as follows: 12 ml of concentrated sulphuric acid and about 5 g of potassium sulphate were added to the samples which had been placed in 500-ml flasks. Funnels with short stems partially closed the flasks. The contents of each flask was heated to the boiling point for 20 minutes. To each flask was then added 250 ml of water and 20 ml of hydrochloric acid and the solution boiled 5 minutes. The contents of each flask was then cooled to 10° C. and titrated with a permanganate solution which had an antimony titre of 0.00340 g. The volumes of permanganate used in the titrations were corrected for the "blank" determinations which required an average volume of 0.08 ml. As a check on the antimony determinations, a number of 0.1 g portions of the Bureau's standard sample of lead-base bearing metal were analyzed and the amounts of antimony found in each determination agreed well with the calculated amounts.

The results in table 5 show that the percentage of antimony found in the active material of the negative plates of cells A to F increased as the antimony content of the positive grids was increased. The commercial grids in cells T, U, and V, however, deposited greater amounts of antimony upon the negative plates. The reason for this is not altogether apparent, but a possible explanation is the fact that these grids had 36 crossbars compared with 27 for the grids in cells A to F. The 36 crossbars were finer in structure than the others, but the corrosion of the grids is probably localized at the surface of the plates and the number is of more significance therefore than the actual area or amount of the metal. Another possible explanation is found in the fact that the outer edges of the crossbars of the commercial grids were much sharper than the others. A nonuniform current distribution between grid and active material would result in an increased current density at the outer edges of these grid bars. This would accelerate the corrosion of these bars.

Although table 5 shows clearly that positive grids containing 9 and 12 percent antimony have deposited appreciably more antimony on the negative plates than those containing 3 and 7 percent of antimony, there is no exact proportionality between the composition of the positive grids and the antimony found in the negative active material after 115 cycles of charge and discharge.

5. RATE OF SULPHATION OF NEGATIVE PLATES

The "local action" produced at the surface of the plates when immersed in solutions of sulphuric acid results in the formation of lead sulphate and consequently a gain in weight of the plates. We have employed an apparatus, referred to previously, to determine the rate of local action when the plates were suspended in solutions of 1.250 specific gravity and maintained at 25° C. The results corrected for buoyancy are given in table 6.

TABLE 6.—*Rate of sulphation of negative plates in sulphuric acid solutions of 1.250 specific gravity at 25° C.*

Cell	Antimony in active material	Final charge		Increase in weight of negative plates			
		Cell	Negative Cd	5 days	10 days	15 days	25 days
	Percent	*Volts*	*Volts*	*g*	*g*	*g*	*g*
A	0.0_4	2.82	−0.25	0.8	1.5	2.0	3.0
C	$.1_1$	2.60	−.10	1.0	1.9	2.7	4.2
D	$.2_4$	2.59	−.06	1.6	3.0	4.2	6.6
E	$.2_6$	2.53	−.02	1.8	3.3	4.7	7.4
F	$.3_2$	2.56	−.02	2.4	4.3	6.1	9.5
V	$.4_1$	2.54	−.02	2.7	4.8	6.9	10.7
U	----------	2.52	−.02	3.3	6.1	8.7	13.5
T	$.4_6$	2.52	.00	3.4	6.5	9.1	13.6

The chemical reaction is believed to take place according to the equation

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2$$

This reaction might also be measured by determining the volume of hydrogen liberated as a result of the reaction. Crennell and Milligan,[24] and others have used such a method. Since the overvoltage for hydrogen discharge on antimony is less than on lead, this reaction will proceed more rapidly when antimony is present in the active material of the plate, provided the antimony is not covered by lead or lead sulphate and thereby rendered ineffective.

The results in table 6 show increased rates of sulphation as the amount of antimony in the active material increased. An exact proportionality between all values does not exist. Grids of similar design but varying in percentages of antimony will liberate antimony in the electrolyte in proportion to the antimony which they contain, provided there is no appreciable difference in the relative rate of corrosion. Antimony will deposit on the negative plates in the same proportion as the amounts set free in the electrolyte. The freshly deposited antimony is therefore proportionately greater on those plates operating in the cells with positives of high antimony content, and the total amount of antimony in the active material of the negative plates is also proportionately greater as was observed in the case of cells D, E, and F. In cell C, however, where the grid corrosion exceeded that in D, E, and F the antimony found in the active material and the rate of sulphation are both more than proportionately greater. It does not follow necessarily that the rate of sulphation is proportional to the total amount of antimony present except as the freshly deposited antimony is also proportional to the total amount.

The results in table 6 show that the rate of sulphation for plates from cell A (which contained positive grids of pure lead) was very small. A gain in weight of 3 g per plate is equivalent to a discharge of 1.68 ampere-hours by local action in 25 days or one fourth the loss in cells T, U, and V which contained plates with the ordinary commercial grids.

Local action on negative plates has been attributed sometimes to certain materials used as expanders. In the present experiments all of the negative plates were pasted with the same materials and the results are comparable. It is evident that local action caused by the expander is small compared with that caused by antimony.

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[24] World Power, vol. 17, p. 406, 1932.

V. CADMIUM SERIES OF EXPERIMENTS

1. CAPACITY DETERMINATIONS

The cells containing positive grids consisting of alloys of lead and cadmium were made and operated in a similar manner to that described in the preceding antimony series of experiments. The composition of the positive grids for these cells is shown in table 7. Most of these cells compared favorably in capacity with the cells of the antimony series until near the end of the experiment. Examination of the plates was made after the hundredth cycle and the condition of the positive plates is described in the last column. The positive grids were all corroded and expanded, except in cells O, P, and S. The negative plates in all cells were in good condition, however. One of the most striking features revealed by the examination of the plates was the formation of compact and adherent moss on the lower part and sides of the elements. This was found in nearly all cells containing cadmium. The moss was removed before continuing the test of these cells.

TABLE 7.—*Capacity of cells having cadmium in positive grids*

Cell	Composition of positive grids			Cycle no. 2	Cycle no. 23	Cycle no. 49	Cycle no. 78	Cycle no. 91	Cycle no. 113	Condition of positive plates
	Lead	Antimony	Cadmium							
	Percent	*Percent*	*Percent*	*Amp.-hr.*	*Amp.-hr.*	*Amp.-hr.*	*Amp.-hr.*	*Amp.-hr.*	*Amp.-hr.*	
A	100	0	0	40	63	68	69	70	72	Corroded, expanded, and cracked.
G	99	0	1	42	63	64	72	65	64	Corroded, expanded, moss.
H	98	0	2	42	63	67	70	74	68	Do.
I	98.75	.25	1	49	63	64	68	62	62	Do.
J	97.75	.25	2	49	63	65	68	72	75	Do.
K	99	.5	.5	51	62	63	70	72	69	Do.
L	98.5	.5	1	42	61	64	66	72	69	Do.
M	97.5	.5	2	51	65	64	69	66	65	Do.
N	98.5	1	.5	40	62	65	74	66	72	Do.
O	97	1	2	42	62	62	64	66	64	Better condition, no moss.
P	97	2	1	42	61	62	62	68	72	Do.
S	96	2	2	42	61	63	66	62	72	Good condition, some moss.

The grids containing cadmium did not give as good service as those containing antimony in the usual amounts. They were distinctly better, however, than grids of lead-bismuth alloys which were tested previously. With improved technic for casting the lead-cadmium alloys, it is possible that such grids could be improved. Corrosion may have been accelerated by slight porosity of the metal. The fact that the plates were formed with the separators present in the element may have been a factor in causing corrosion. Corrosion of grids has been found to be serious when minute amounts of volatile organic acids have direct access to the bare metal during charge. Lead sulphate affords little protection to lead against the attack of such acids, but lead dioxide, when formed, is a much more effective covering.

2. RATE OF SULPHATION OF NEGATIVE PLATES

Experiments on the rate of sulphation of the negative plates after 115 cycles were made similarly to those reported for the antimony series. The results are given in table 8. The contrast between the results in this table and those in table 6 for the cells containing antimony grids is very marked. The increase in weight of the plates (table 8) because of the formation of lead sulphate is less in every case than for any cell in table 6 with the single exception of cell A, which contained no antimony. At the same rate of local action some of these plates could have stood for a year without being completely discharged.

TABLE 8.—*Rate of sulphation of negative plates in sulphuric-acid solutions of 1.250 specific gravity at 25° C.*

Cell	Increase in weight of negative plates				Cell	Increase in weight of negative plates			
	5 days	10 days	15 days	25 days		5 days	10 days	15 days	25 days
	g	g	g	g		g	g	g	g
A	0.8	1.5	2.0	3.0	M	0.6	1.1	1.7	2.5
G	.7	1.4	1.9	2.9	P	.8	1.4	1.8	2.7
H	.6	1.1	1.5	2.4	S	.9	1.7	2.3	3.5
L	.7	1.3	1.8	2.8					

VI. DISCUSSION OF RESULTS

The higher rate of sulphation of negative plates previously cycled with positives whose grids contain antimony in customary amounts, compared with the negligible rate of sulphation of similar plates cycled with pure-lead positives or those containing little or no antimony, is convincing evidence that the composition of the positive grids is an important factor influencing the operation of the negative plates. The effects of antimony on the negative plates are not the result of exceptional conditions, but may be expected in the ordinary conditions of operation of batteries.

Some of the advantages to be gained in the operation of negative plates by curtailing the use of antimony in the positive plates are: (*a*) Longer life of the negative plates in service; (*b*) more uniform cell voltages and plate potentials during the life of the cell; (*c*) less local action at the negative plates when battery is inactive; (*d*) less occasion for overcharging batteries, because of less sulphation of the negatives; and (*e*) less possibility for the formation of stibine when hydrogen is discharged on antimony.

To gain such advantages for the negative plates, however, requires the solution of difficult problems regarding the construction of the positive plates.

VII. SUMMARY

The effect of antimony in producing excessive sulphation of negative plates in storage batteries has been known previously, but recent experiments at the Bureau of Standards and elsewhere have shown that the small amounts of antimony released from the positive grids in the course of normal operation of batteries are sufficient to affect the negative plates.

Batteries have been made and operated in the laboratory to test the effect of varying the composition of the grids for positive plates. The alloys, which were employed in this work, included a series of lead-antimony and lead-cadmium compositions.

The operation of the batteries was observed during 115 cycles of charge and discharge. For the most part, the cycling of the batteries was controlled automatically, but measurements of capacity and plate potentials were made at intervals during the course of the tests.

No large differences in capacity resulted from variations in the antimony content of the positive grids, but grids containing 3 percent or less of antimony were not as durable as those of customary compositions.

Tests for loss of charge on standing for a period of 114 days showed the loss to be greater in those cells containing the higher percentages of antimony in the positive grids. The capacity of the cells, with one exception, was limited by the negative plates, however, and these were found to contain measurable quantities of antimony in the active material after completing 115 cycles of charge and discharge.

The percentage of antimony found by analysis in the active material of the negative plates was greater in those cells whose positive grids contained the greater percentages of antimony. The analysis for antimony was made at the conclusion of 115 cycles of charge and discharge.

Local action produced at the surface of the negative plates was measured by weighing the plates at intervals while they were suspended in solutions of sulphuric acid and maintained at a constant temperature. The plates having the greatest amount of antimony in the active material sulphated the most rapidly. The negative plates from cells whose positive grids were made of pure lead or the lead-cadmium alloys sulphated less than the others.

Positive grids of lead-cadmium alloys did not prove to be as durable as the lead-antimony alloys in these experiments. The operation of negative plates was improved, however, by the absence of antimony from the positive grids. Part of the difficulty with the lead-cadmium alloys may have been caused by insufficient experience in using such material in batteries.

VIII. ACKNOWLEDGMENT

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